

Hydrogen and Hydrocarbon Oxidation

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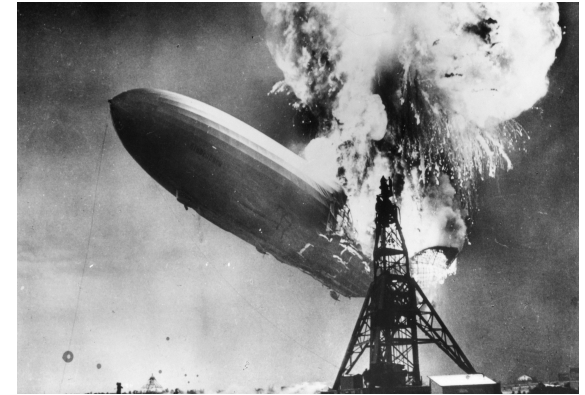


Reaction Mechanisms

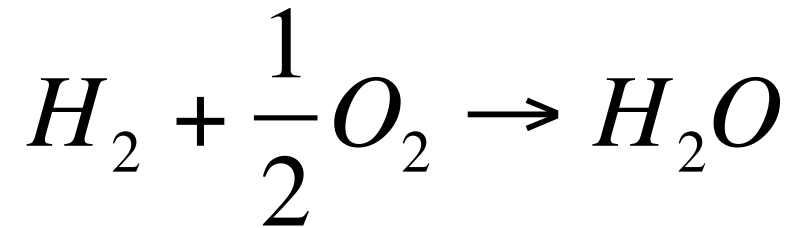
- We now delve into some practical kinetic reaction mechanisms.
- Such a mechanism specifies all species, all thermodynamic and transport properties, and all reactions and rates.
- We start with the simplest combustion system, the oxidation of hydrogen.

H₂/O₂ Combustion

- H₂/O₂ combustion chemistry is important
 - H₂/O₂ mixture can be highly explosive
 - H₂/O₂ combustion important in own right (rocket propulsion, low emission vehicles, fuel cells)
 - H₂/O₂ reaction mechanism is the underpinning to virtually all hydrocarbon chemistry



- The global reaction is:



- Studied for over two centuries (Sir Humphry Davy).
- General behavior well established by the early twentieth century.
- The heat of combustion for this reaction is 141,800 kJ/kg (HHV), which is two to three times that of other common fuels like gasoline.

Table I. Detailed H₂/O₂ Reaction Mechanism. Units are cm³-mol-sec-kcal-K, and $k = A T^n \exp(-E/RT)$.

		A	n	E	Reference
<i>H₂/O₂ Chain Reactions</i>					
1.	H + O ₂ = O + OH	3.55 × 10 ¹³	-0.41	16.6	Hessler [16]
2.	O + H ₂ = H + OH	5.08 × 10 ⁶	2.67	6.29	Sutherland et al. [44]
3.	H ₂ + OH = H ₂ O + H	2.16 × 10 ⁸	1.51	3.43	Michael et al. [45]
4.	O + H ₂ O = OH + OH	2.97 × 10 ⁶	2.02	13.4	Sutherland et al. [46]
<i>H₂/O₂ Dissociation/Recombination Reactions</i>					
5.	H ₂ + M = H + H + M ^a	4.58 × 10 ¹⁹	-1.40	104.38	Tsang et al. [47]
	H ₂ + Ar = H + H + Ar	5.84 × 10 ¹⁸	-1.10	104.38	Tsang et al. [47]
	H ₂ + He = H + H + He	5.84 × 10 ¹⁸	-1.10	104.38	See text
6.	O + O + M = O ₂ + M ^a	6.16 × 10 ¹³	-0.50	0.00	Tsang et al. [47]
	O + O + Ar = O ₂ + Ar	1.89 × 10 ¹³	0.00	-1.79	Tsang et al. [47]
	O + O + He = O ₂ + He	1.89 × 10 ¹³	0.00	-1.79	See text
7.	O + H + M = OH + M ^a	4.71 × 10 ¹⁸	-1.0	0.00	Tsang et al. [47]
8.	H + OH + M = H ₂ O + M ^b	3.8 × 10 ²²	-2.00	0.00	See text
<i>Formation and Consumption of HO₂</i>					
9.	H + O ₂ + M = HO ₂ + M ^a	k _O 6.37 × 10 ¹⁹	-1.72	0.52	Michael et al. [19] (M = N ₂)
	H + O ₂ + M = HO ₂ + M ^a	k _O 9.04 × 10 ¹⁹	-1.50	0.49	Michael et al. [19] (M = Ar or He)
		k _{He} 1.48 × 10 ²²	0.60	0.00	Cobos et al. [48]
10.	HO ₂ + H = H ₂ + O ₂	1.66 × 10 ¹³	0.00	0.82	Mueller et al. [1]
11.	HO ₂ + H = OH + OH	7.08 × 10 ¹³	0.00	0.30	Mueller et al. [1]
12.	HO ₂ + O = OH + O ₂	3.25 × 10 ¹³	0.00	0.00	Baulch et al. [34]
13.	HO ₂ + OH = H ₂ O + O ₂	2.89 × 10 ¹³	0.00	-0.50	Baulch et al. [34]
<i>Formation and Consumption of H₂O₂</i>					
14.	HO ₂ + HO ₂ = H ₂ O ₂ + O ₂ ^a	4.20 × 10 ¹⁴	0.00	11.98	Hippler et al. [49]
	HO ₂ + HO ₂ = H ₂ O ₂ + O ₂	1.30 × 10 ¹¹	0.00	-1.63	
15.	H ₂ O ₂ + M = OH + OH + M ^c	k _O 1.20 × 10 ¹⁷	0.00	45.5	Warnatz [50]
		k _{He} 2.95 × 10 ¹⁴	0.00	48.4	Brouwer et al. [51]
16.	H ₂ O ₂ + H = H ₂ O + OH	2.41 × 10 ¹³	0.00	3.97	Tsang et al. [47]
17.	H ₂ O ₂ + H = H ₂ + HO ₂	4.82 × 10 ¹³	0.00	7.95	Tsang et al. [47]
18.	H ₂ O ₂ + O = OH + HO ₂	9.55 × 10 ⁶	2.00	3.97	Tsang et al. [47]
19.	H ₂ O ₂ + OH = H ₂ O + HO ₂ ^a	1.00 × 10 ¹²	0.00	0.00	Hippler et al. [52]
	H ₂ O ₂ + OH = H ₂ O + HO ₂	5.8 × 10 ¹⁴	0.00	9.56	

^aEfficiency factors are: $\epsilon_{\text{H}_2\text{O}} = 12.0$, $\epsilon_{\text{H}_2} = 2.5$, $\epsilon_{\text{Ar}} = 0.75$, and $\epsilon_{\text{He}} = 0.75$. When a rate constant is declared specifically for Ar or He collision partner, the efficiency of Ar or He is set to zero when determining M for the same reaction.

^bEfficiency factors are: $\epsilon_{\text{H}_2\text{O}} = 12.0$, $\epsilon_{\text{H}_2} = 2.5$, $\epsilon_{\text{Ar}} = 0.38$, and $\epsilon_{\text{He}} = 0.38$.

^cWhen the main bath gas is N₂. Troe parameter is: $F_c = 0.8$. Efficiency factors are: $\epsilon_{\text{H}_2\text{O}} = 11.0$, $\epsilon_{\text{H}_2} = 2.0$, and $\epsilon_{\text{O}_2} = 0.78$.

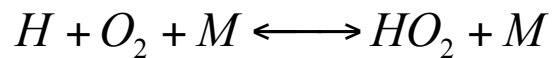
Example of an
H₂/O₂ reaction
mechanism.

Li, Z. Zhao, A. Kazakov, F.L.
Dryer, Int. J. Chem. Kin. 36
(2004) 566-575.

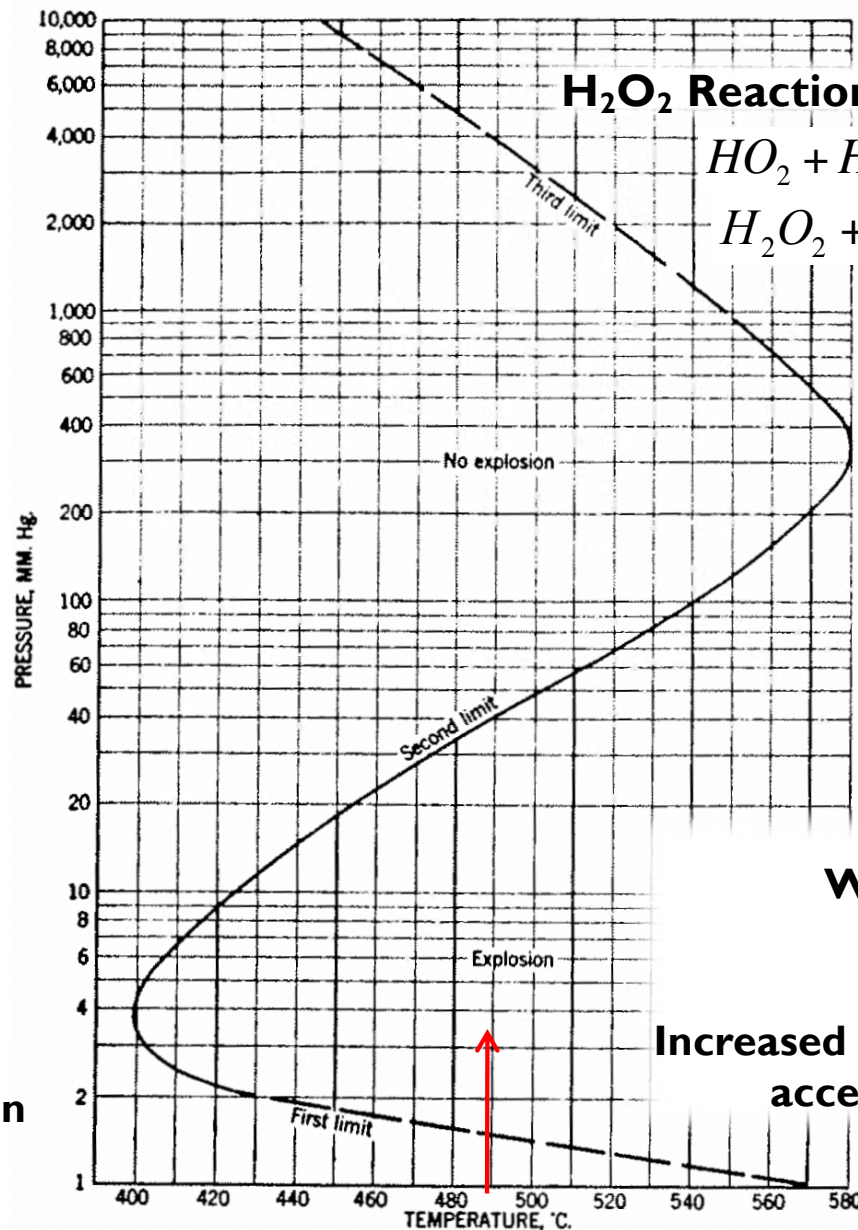


H₂/O₂ Explosion Behavior

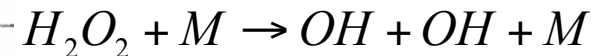
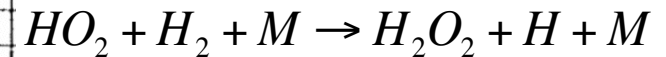
Three body recombination reactions increase
Result: **Slow Combustion**



Radicals destroyed on
vessel walls



H₂O₂ Reaction Increase Chain Branching:

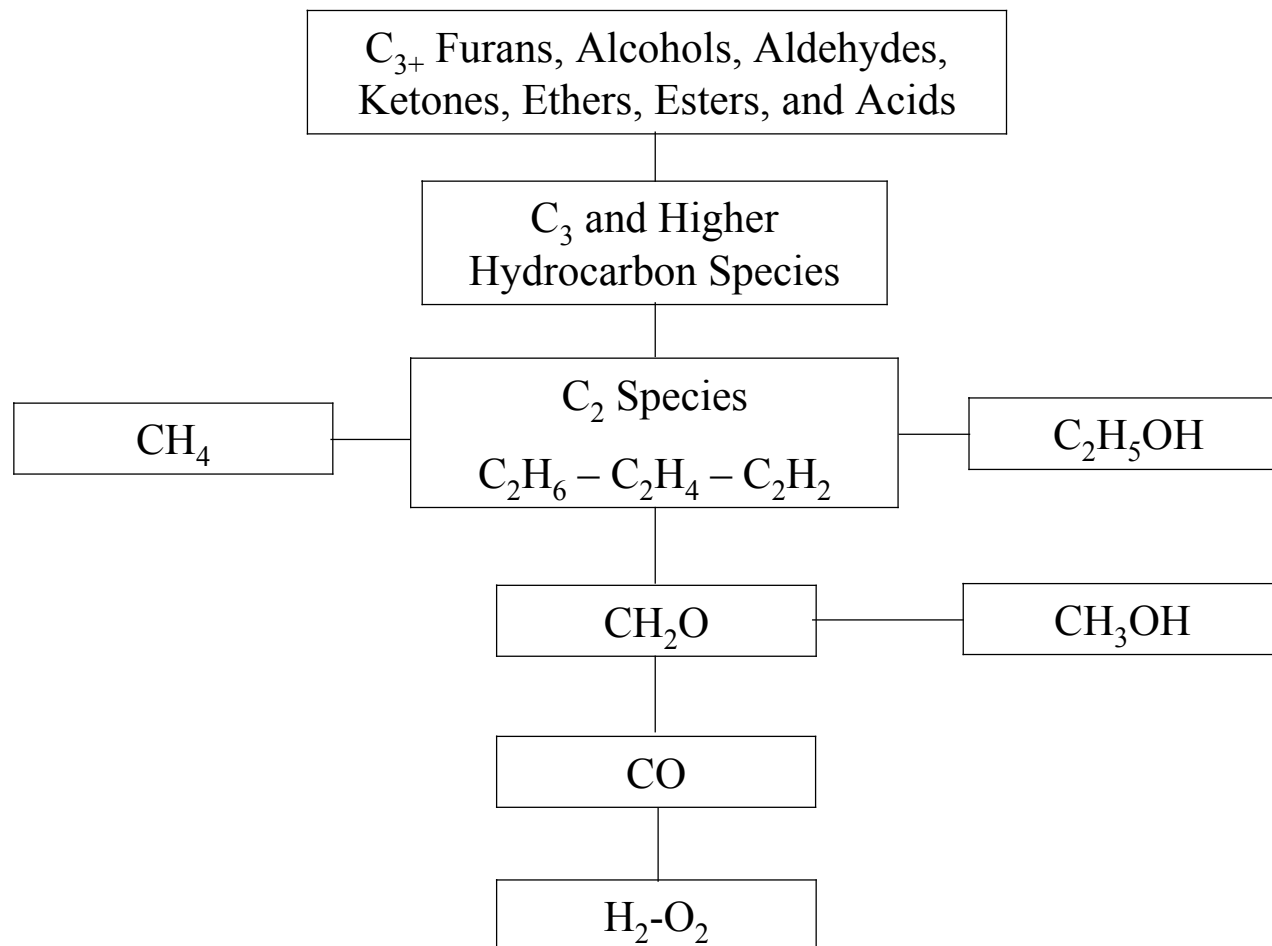


Increased pressure:
Wall diffusion inhibited

Result:

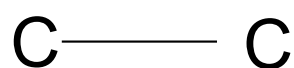
**Increased chain branching reactions and
acceleration of reaction rate**

Hierarchical Structure for Oxidation of Simple Hydrocarbon Fuels

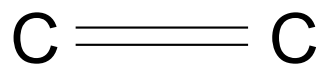


Hydrocarbon Compounds

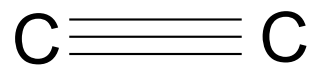
- Alkanes - Single bonds
- Alkenes - Double bonds involved
- Alkynes - Triple bonds involved
- Arines (Aromatic compounds) - Rings



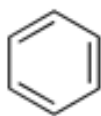
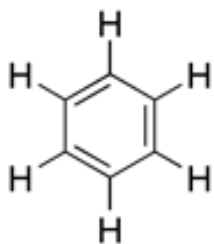
Ethane



Ethene



Ethyne
(Acetylene)



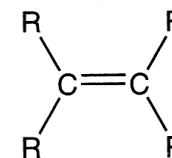
Benzene

Some Common Functional Groups

Alkane



Alkene



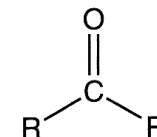
Alkyne



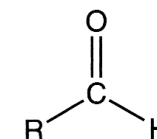
Alcohol



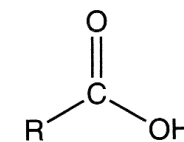
Ketone



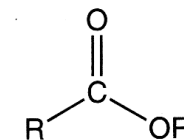
Aldehyde



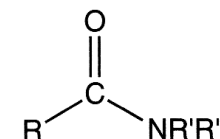
Carboxylic Acid



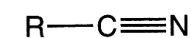
Ester



Amide

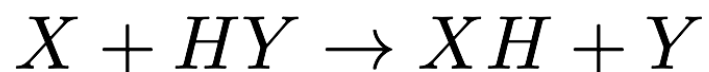


Nitrile

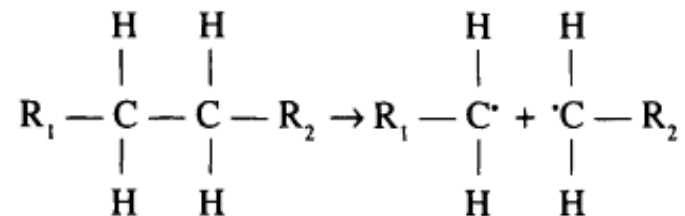


Types of Reactions

- Hydrogen Abstraction



- Beta Scission (means breaking between 2nd and 3rd carbons.

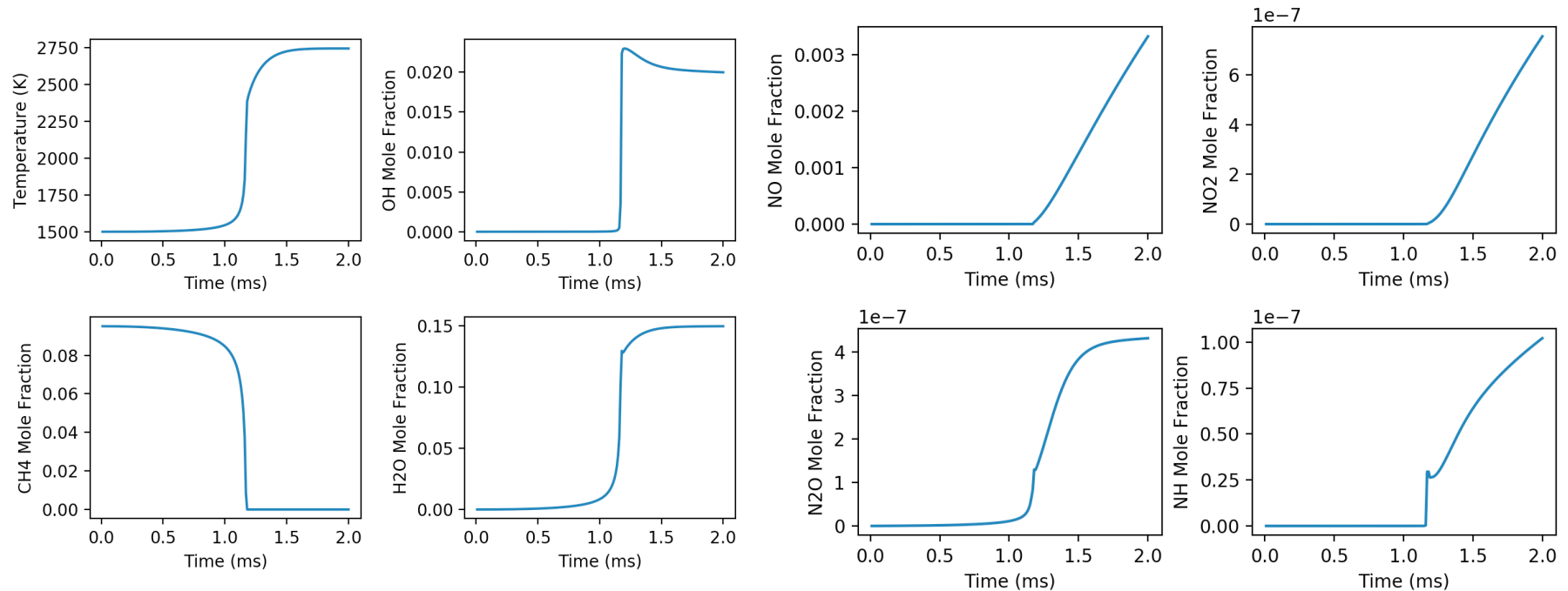


- Unimolecular



Example

- GRIMech_3.0
 - Designed for natural gas combustion
 - 53 species, 325 reactions



Sources of Major Mechanisms

- GRI Mech
 - <http://combustion.berkeley.edu/gri-mech/version30/text30.html>
- LLNL
 - <https://combustion.llnl.gov>
- NIST
 - <http://kinetics.nist.gov>
- Cal Tech Site
 - <https://www.theforce.caltech.edu//CaltechMech/>
- CRECK
 - <http://creckmodeling.chem.polimi.it>
- Plus many more.